

Materials structures for 21st century energy needs

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X-Ray Operations and Research

Advanced Photon Source

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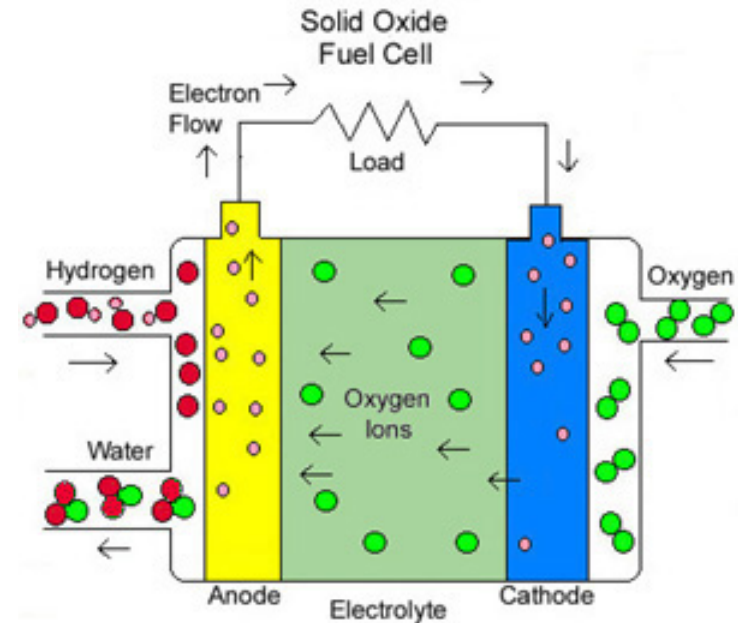
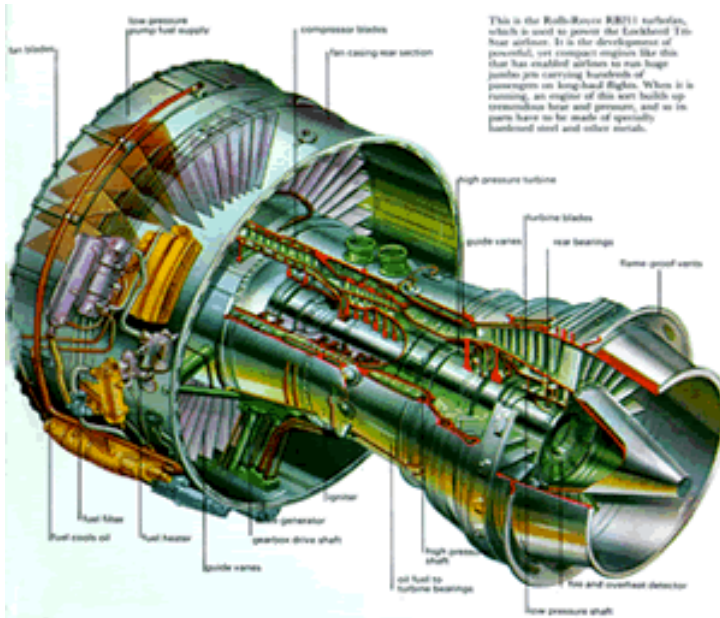
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Advanced ceramic materials in energy utilization



Most of the internal (hot environment) parts in jet engines are coated.
Plasma sprayed or EBPVD (DVD).

Environment friendly, efficient electric energy source.
Functional ceramic layers.
Trends – lower operating temperatures & increase life. Electrolyte reliability is important.



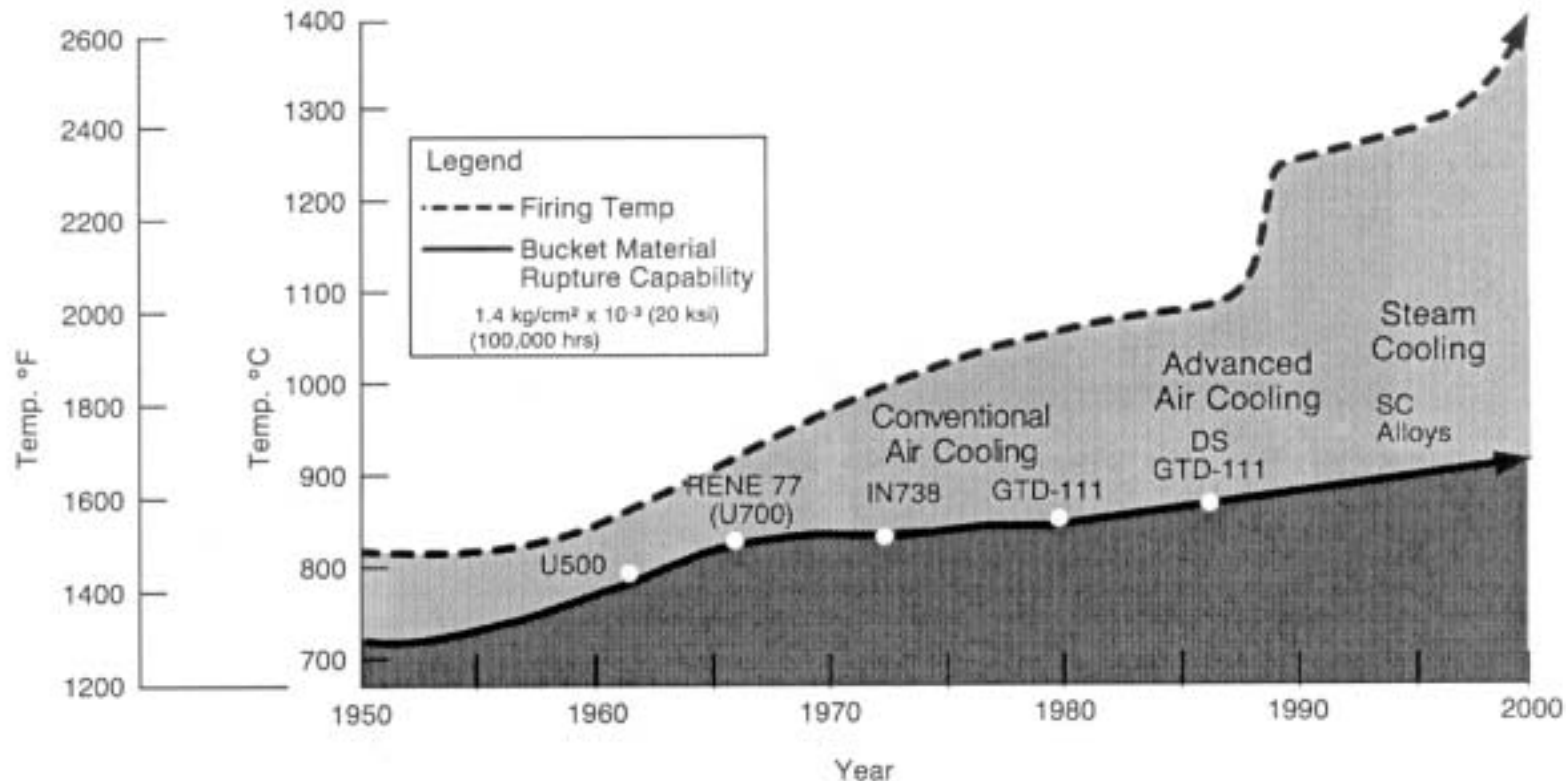
Common

- **Ceramic (cermet) materials.**
- **Microstructure controls the in-service performance.**
- **Need to control/improve:**
 - Functional properties
 - Reliability
 - Predict failure
- **Complex void microstructures – challenge to characterize. Wide size range of voids, possibly anisotropic.**
- **Complex manufacturing processes with high variability of processing parameters.**
- **In-service conditions are severe – high temperature, temperature cycling, chemical effects, erosion → changes of microstructure and therefore performance.**
- **Need to understand microstructure – properties relationships.**



Thermal Barrier Coatings

- Method to increase efficiency of turbine engines (~50°C already)
- Single most potential gain if these can be considered “prime reliant”

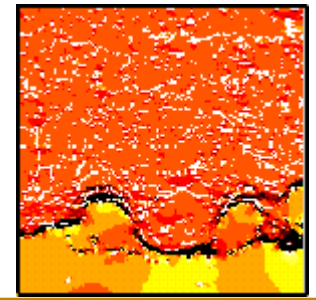
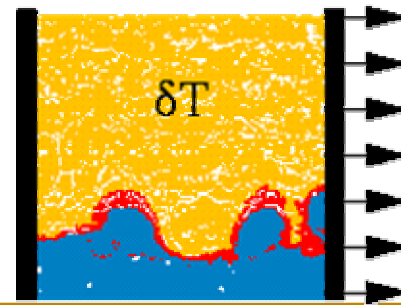
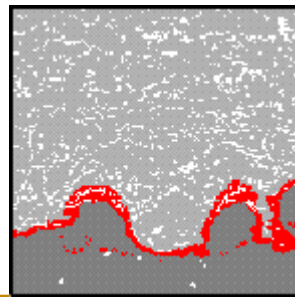
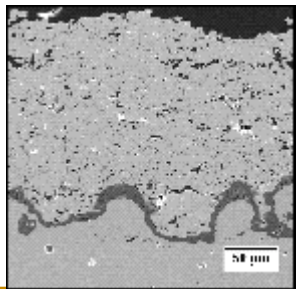


Computer Modeling

- **Engineering development by computer modeling:**
 - Faster
 - More economical
 - Preferred method
- **However:**
 - Materials properties are difficult to obtain (measure) for complex microstructures like advanced ceramic layered structures.
- **Need to establish appropriate set of “descriptors” for microstructure (porosity volume, anisotropy, size distribution..)**
- **Need to understand relationships between:**
 - Processing parameters and microstructure
 - Microstructure and engineering properties (hardness, elastic modulus, thermal conductivity...)

Microstructure – properties relationships modeling

- Develop suitable computer models to link the microstructure to performance properties and the other way.
- Various computer models and methods being developed mostly based on finite element modeling - example “OOF” (NIST)...
 - Input data for now SEM/OM image (2d, limited resolution)
 - Model capable solving problems in 3d, but limited input data available in 3d
 - Tomography is naturally 3d with input format very close to 2d images (both are density maps) – simple transition to new input data



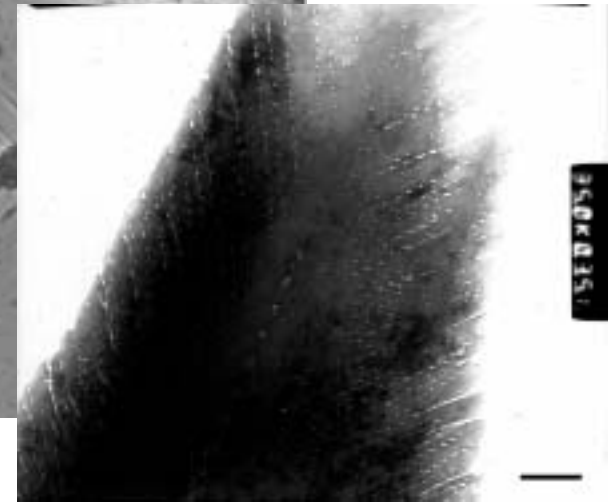
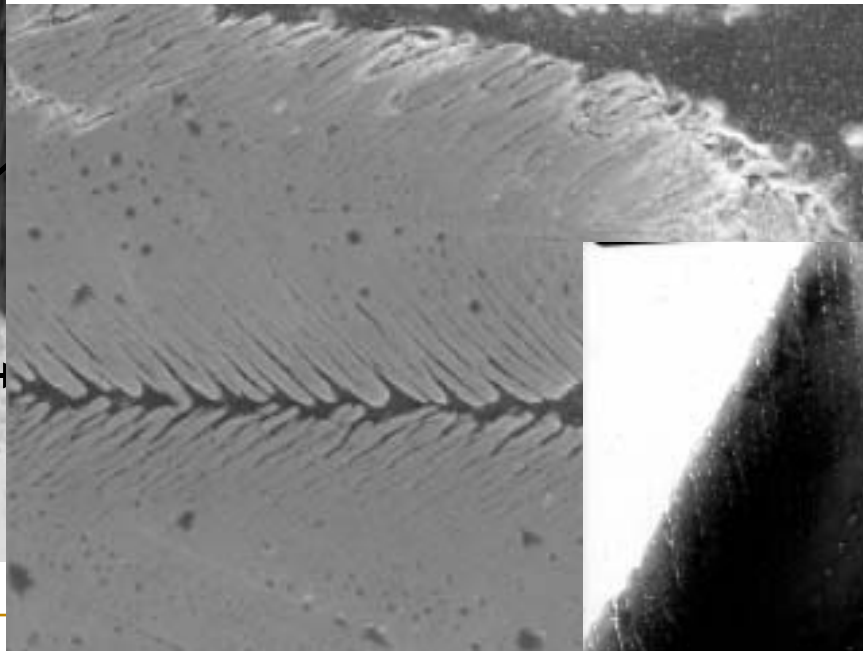
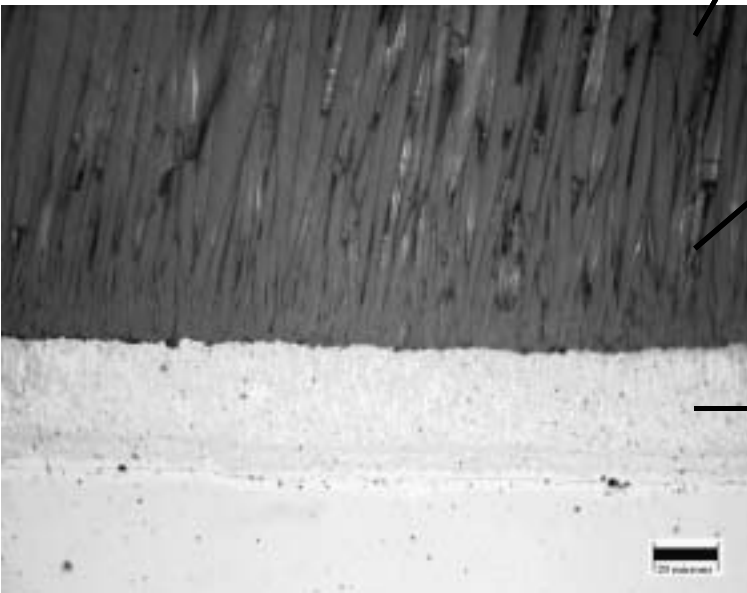
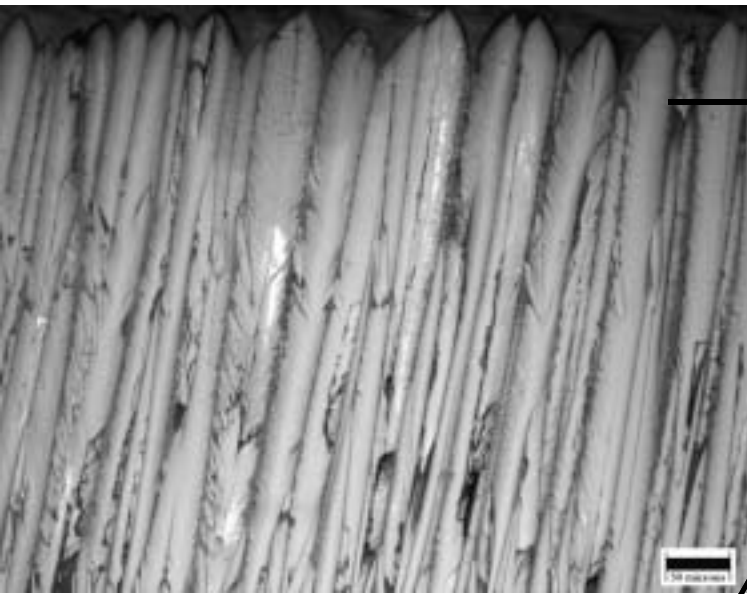
Experiment

- **No single technique available to cover range of voids in the microstructure – from nanometers to number of micrometers**
- **Combined number of techniques:**
 - SEM, OM, TEM
 - Intrusion porosimetry
 - Small-angle scattering (USAXS)
 - Tomography
- **Using microscopy develop microstructure model**
- **Total volume of porosity from intrusion porosimetry**
- **Evaluate USAXS data with this model**
 - Quantitative and statistically representative ($\sim 0.1 - 0.15 \text{ mm}^3$)
 - Nanometers to about 1 micrometer
- **Tomography for larger features**
 - Currently features larger than 1.5 - 2 micrometers
- **>>>>Combine to create “mosaic” or “puzzle” picture of microstructure <<<<**



EBPVD YSZ thermal barrier coatings

- Columnar structure
- “Feather-like” pores within columns
- Change of microstructure through thickness
- Usual thickness about 400 μm , up to 1 mm
- In service changes – sintering and cracking during thermal cycling



Microstructural model for USAXS data analysis

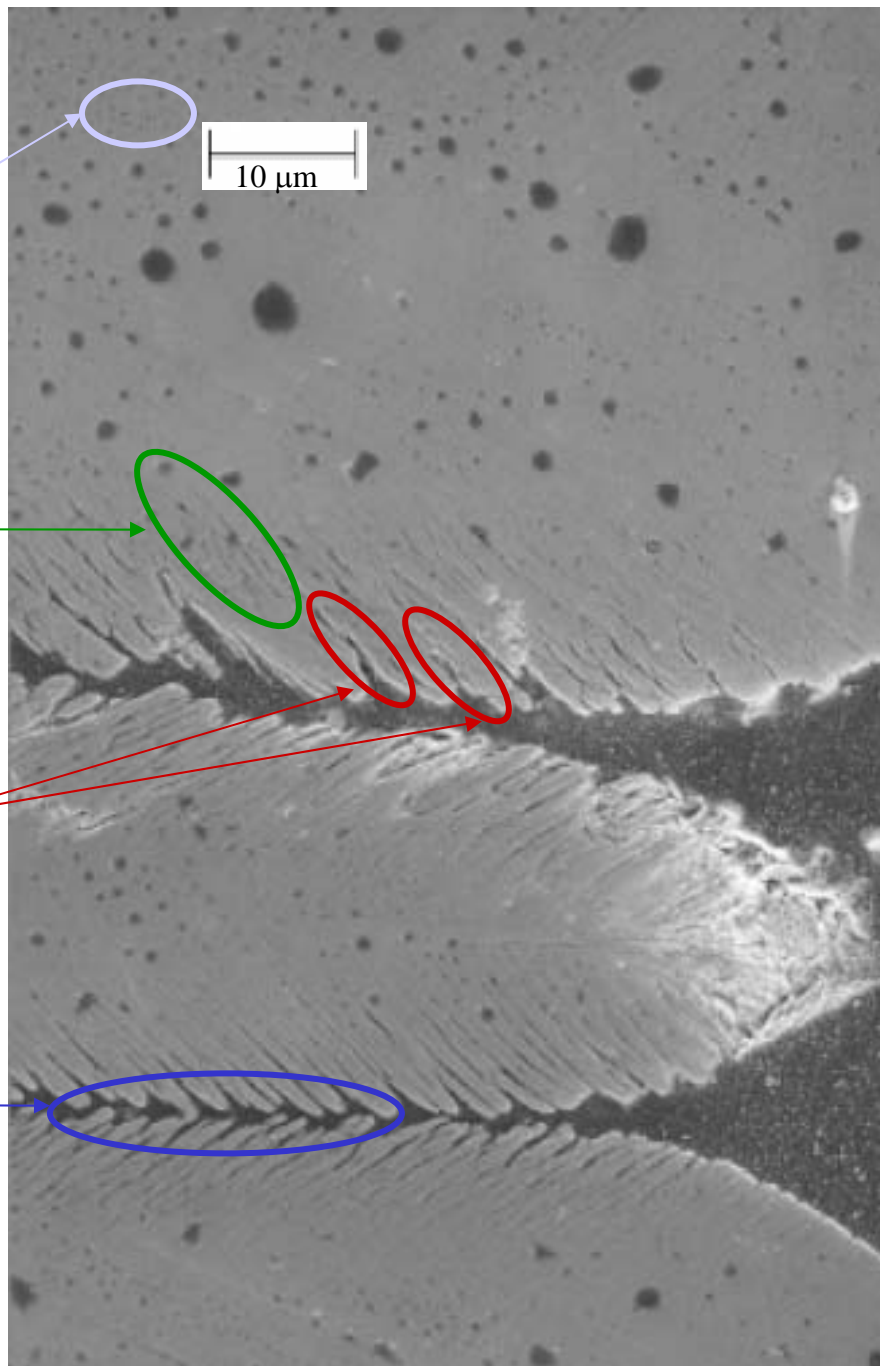
- **For EBPVD (or DVD) thermal barrier coatings**
- **Microstructure composed of 4 populations:**
 - Intercolumnar pores (large, mostly perpendicular to the surface)
 - Intracolumnar pores:
 - *Two populations of feather-like pores*
 - *Population of semi-spherical voids*
- **Features and parameters:**
 - Independent size, aspect ratio, contrast, orientation distribution
 - Dilute limit approximation
 - Simplified size distribution assigned to each population
 - Diffraction & refraction accounted for
 - Allows least square fitting of parameters
- **Complex USAXS data collection (2D collimated) – need to collect many measurements to describe the strong anisotropy:**
 - About 12 hours/sample data collection
 - Few days/sample data analysis

Population 4:
Nano-
Globular
Voids
<o.d.>=0.039 μm
8.7%

Population 3:
Fine
Intracolumnar
Voids
<o.d.>=0.033 μm
3.8%

Population 2:
Coarse
Intracolumnar
Voids
<o.d.>=0.19 μm
3.9%

Population 1:
Intercolumnar
Voids
<o.d.>=0.72 μm
6.1%



TOTAL POROSITY:
22.56 %

(1) INTERCOLUMNAR PORES:
POROSITY: $6.1 \pm 0.6 \%$
<O.D.>: $722 \pm 7 \text{ nm}$
[Aspect Ratio = 0.110, 85° to substrate]

(2) COARSE 'FEATHER' PORES:
POROSITY: $3.9 \pm 0.4 \%$
<O.D.>: $191 \pm 20 \text{ nm}$
[Aspect Ratio = 0.068, 49° to substrate]

(3) FINE nm-PORES:
POROSITY: $3.8 \pm 0.4 \%$
<O.D.>: $33 \pm 4 \text{ nm}$
[Aspect Ratio = 0.050, 49° to substrate]

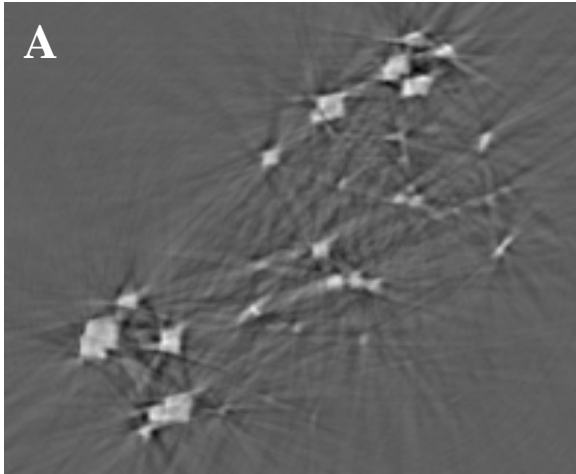
(4) GLOBULAR nm-PORES:
POROSITY: $8.7 \pm 0.9 \%$
DIAMETER: $39 \pm 4 \text{ nm}$
[MEAN DIMENSIONS = $39.1 \times 39.1 \times 27.4 \text{ nm}$]

Tomography

- **Used 2BM tomography at XOR**
- **About 1 – 1.5 micrometers resolution**
- **Sample size**
 - about 150 x 150 micrometers cross section
 - 1 mm height
- **Data set collection – about 15 minutes**



Tomography of EBPVD Zirconia



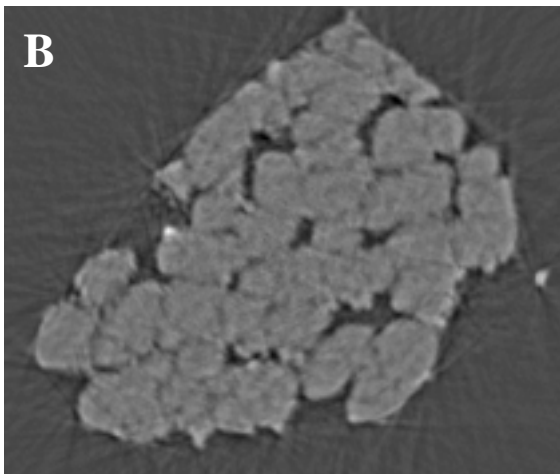
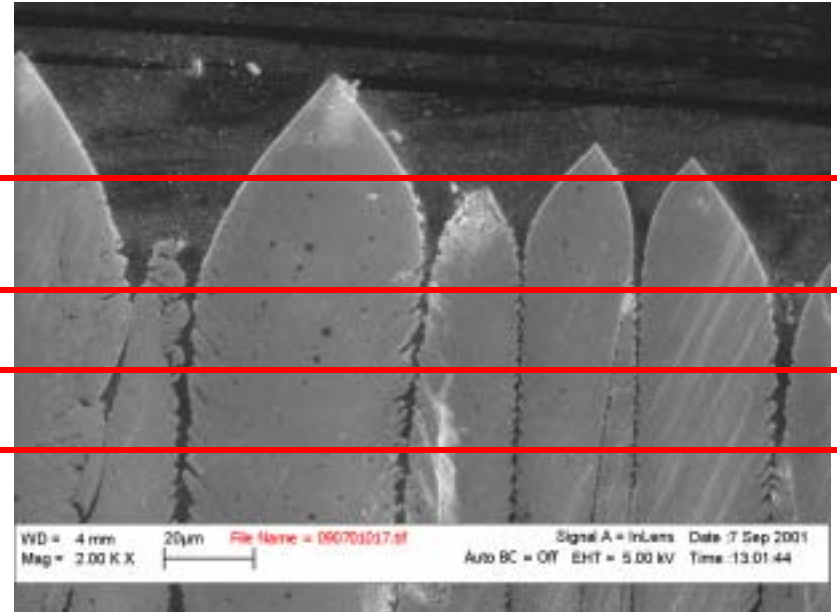
Slice 969

A

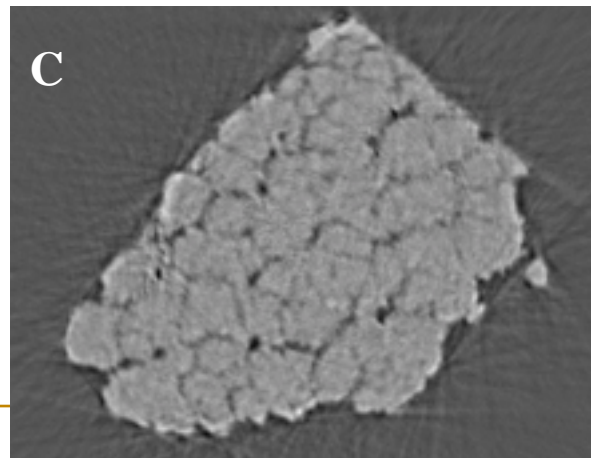
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C

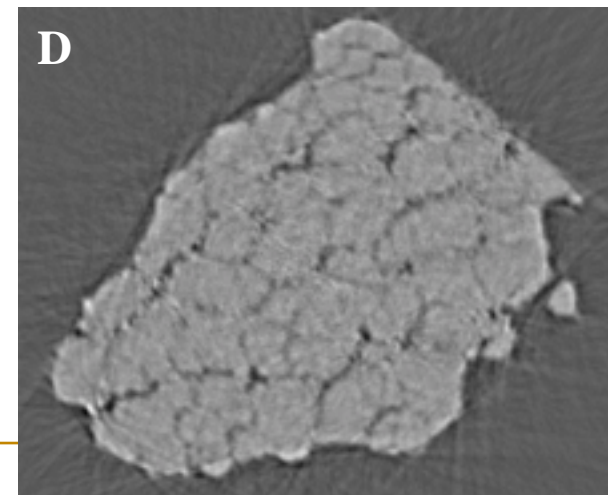
D



Slice 920



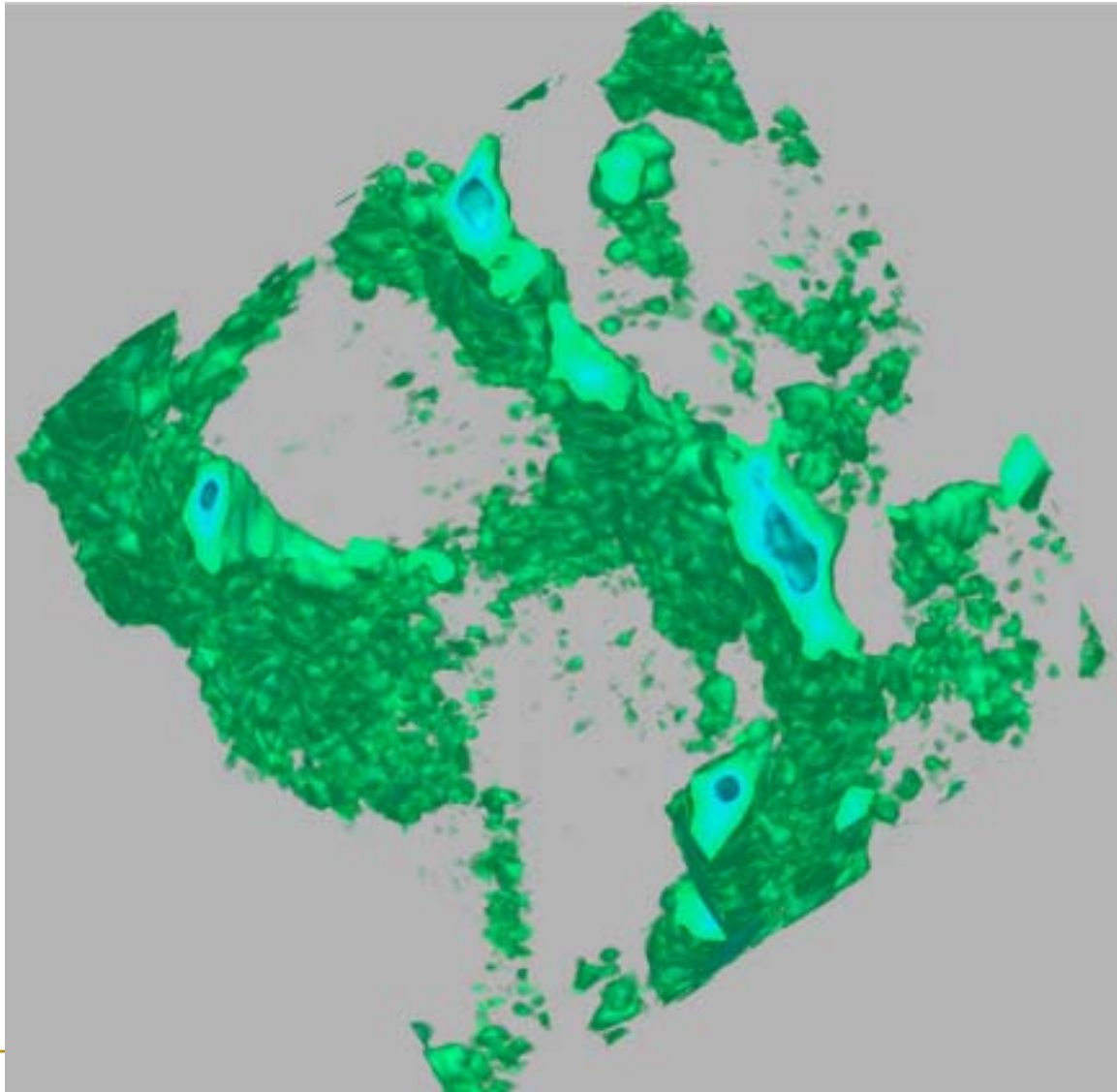
Slice 875



Slice 805

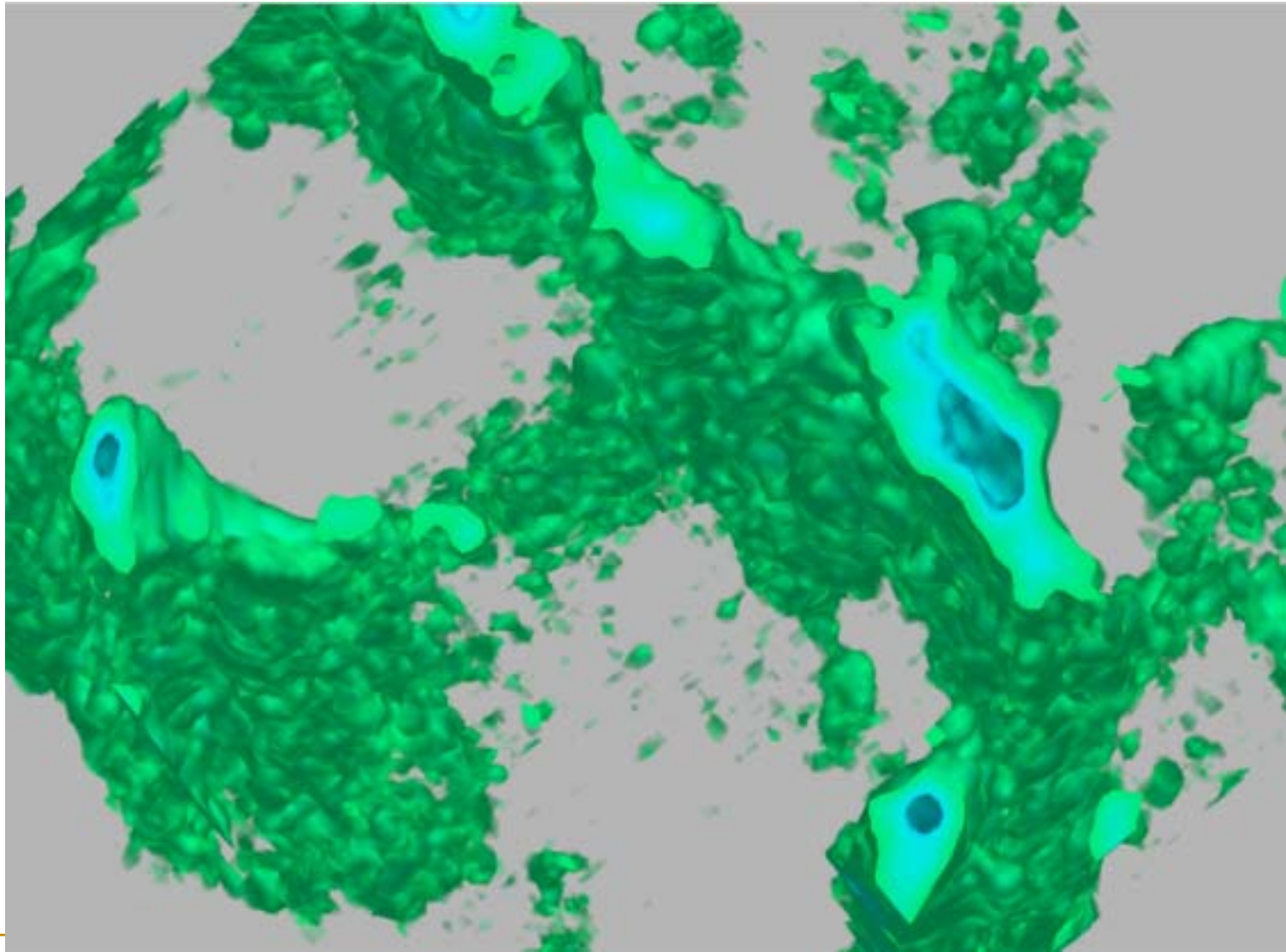
Inverted Image: 3D Pore Morphology in EBPVD TBCs

Top-View

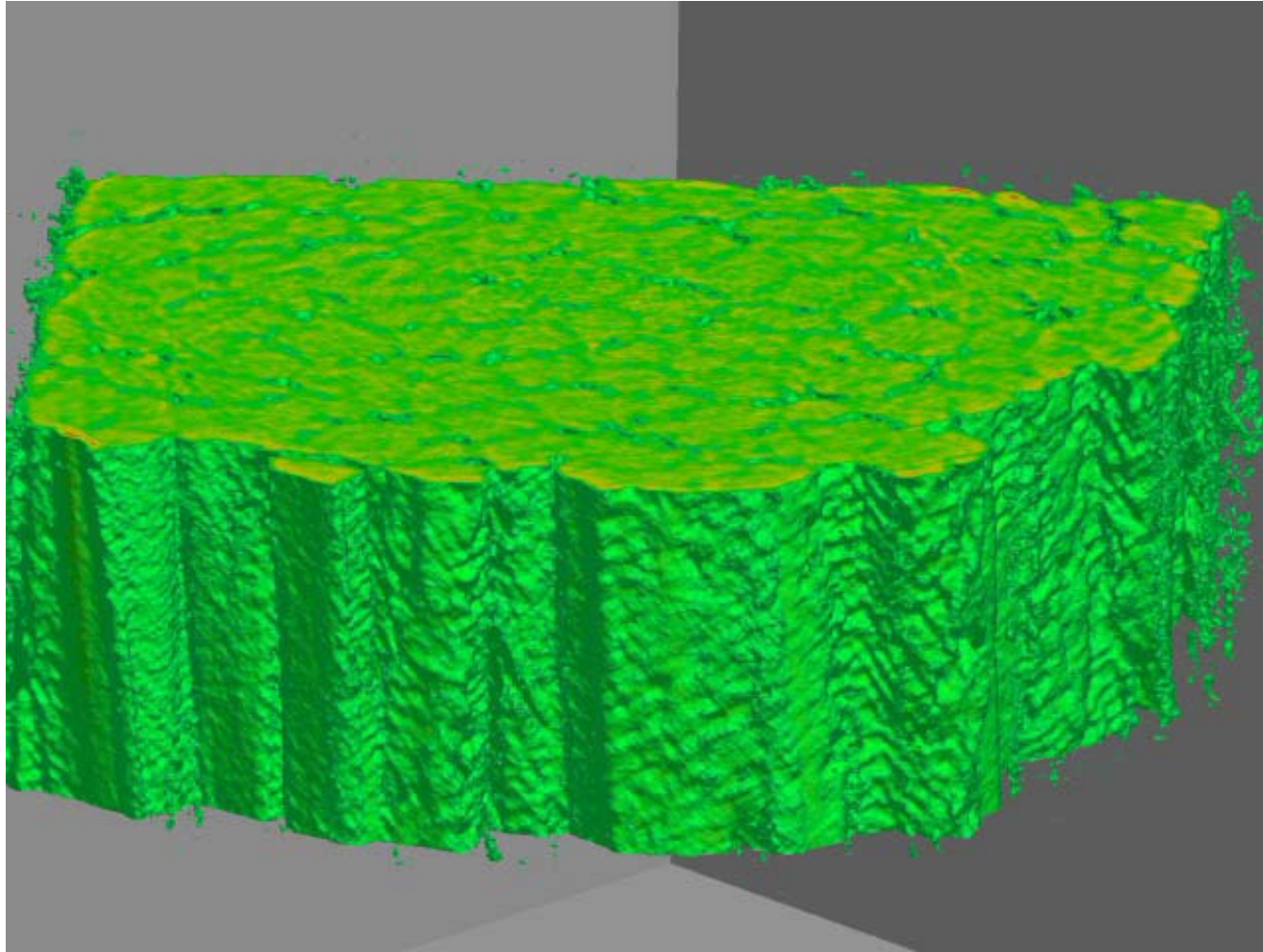


Inverted Image: 3D Pore Morphology in EBPVD TBCs

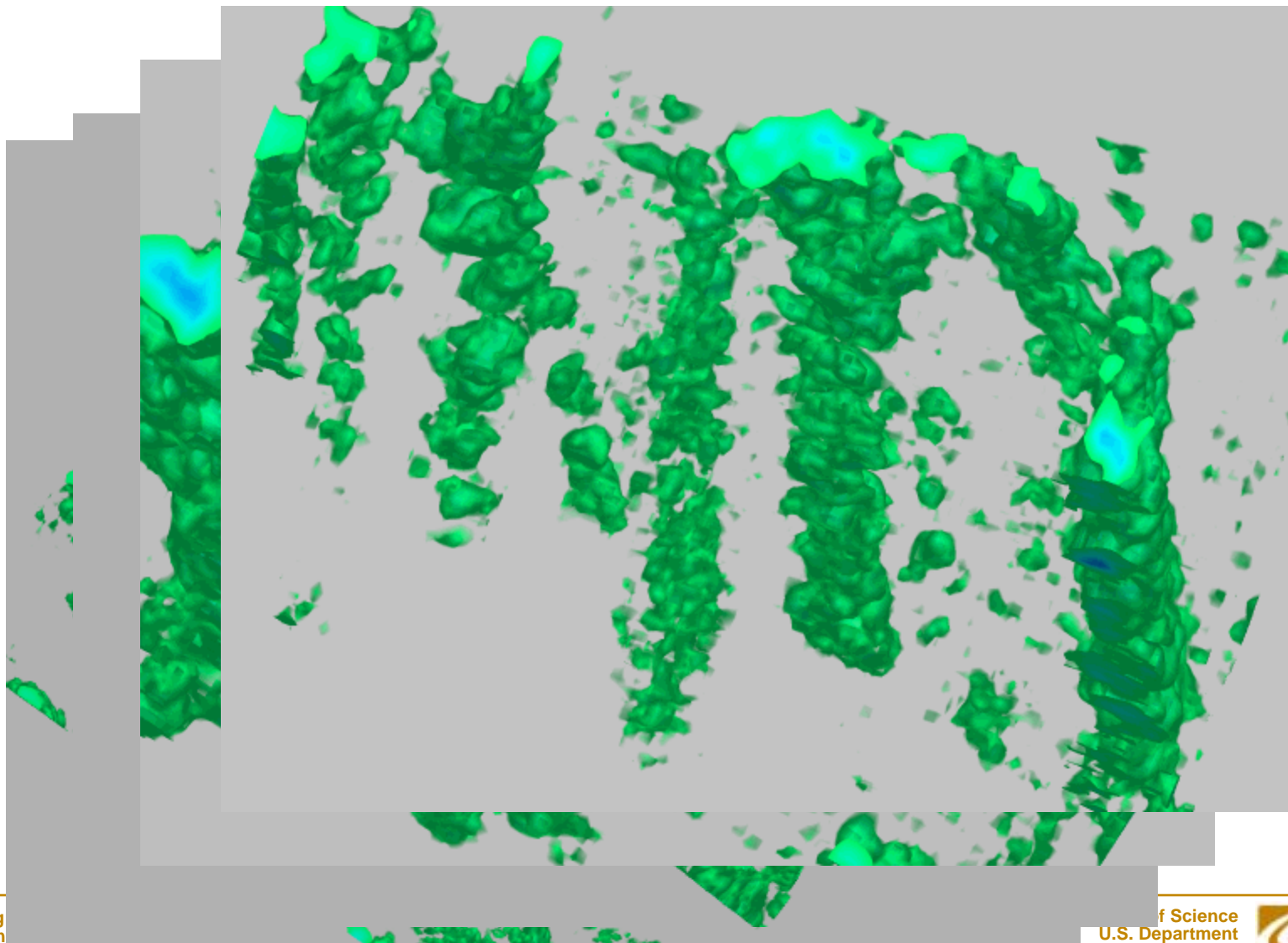
Top-View



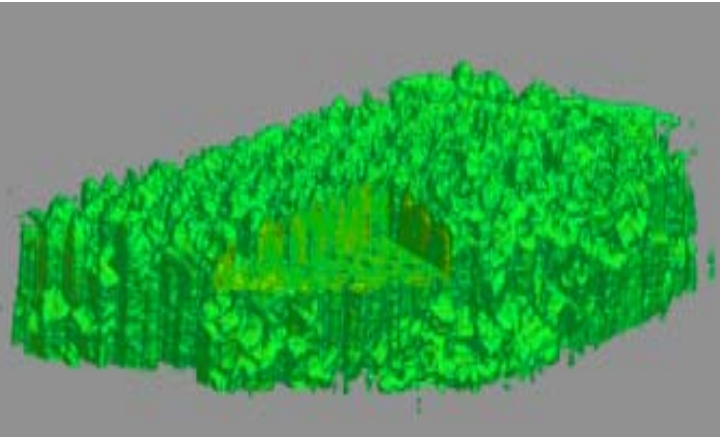
Tomographic visualization EBPVD



Details

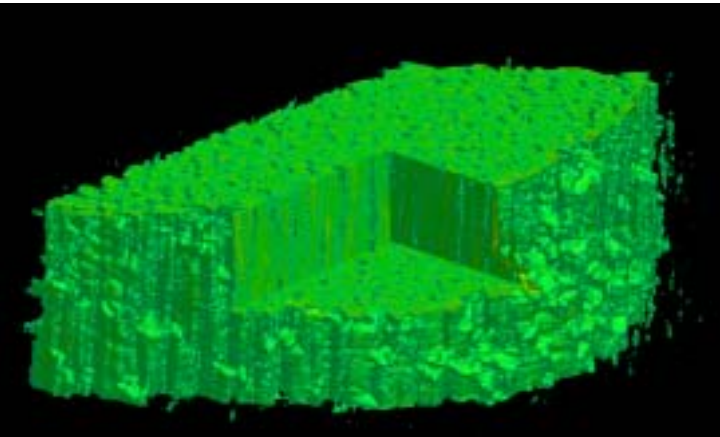
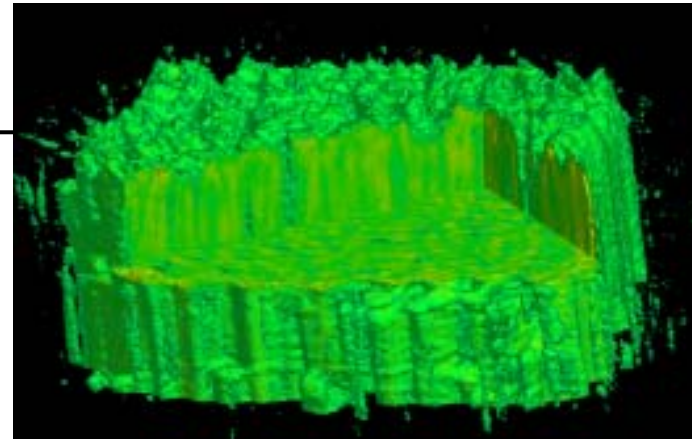


3D Pore Morphology in EBPVD TBCs

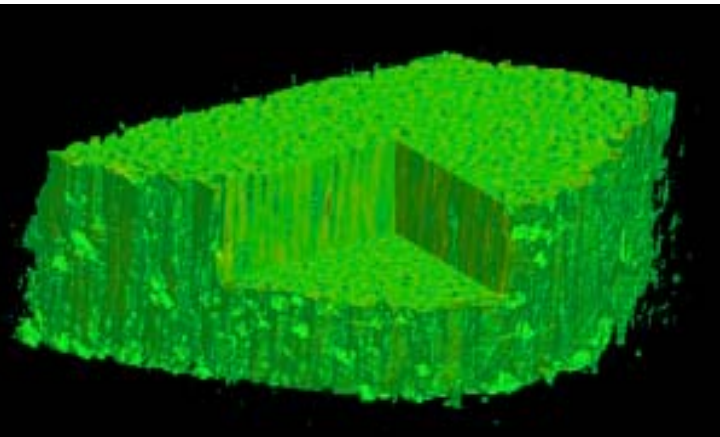
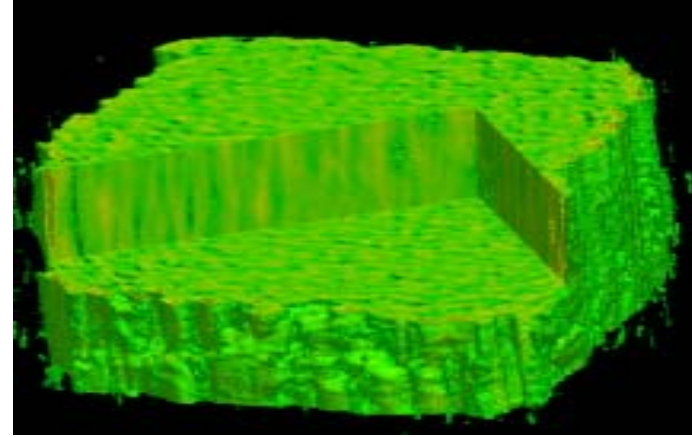


**Sintering effects in
isothermal exposure
(1200°C/550 hrs)**

100 slices,
150 microns thick
1-1.5 μm resolution

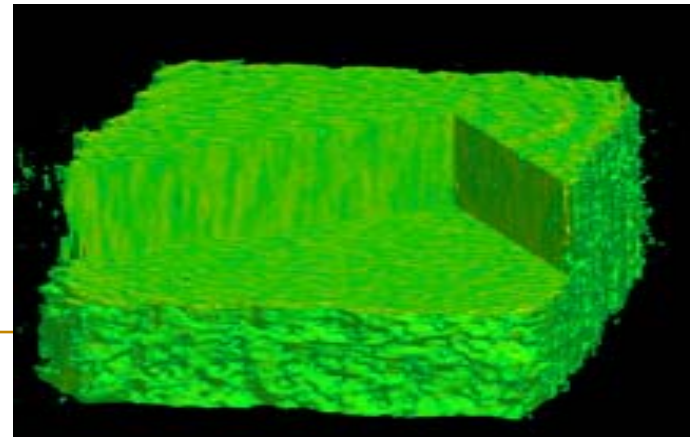


**Columnar pore
morphology**



**Competition zone,
fine pore morphology**

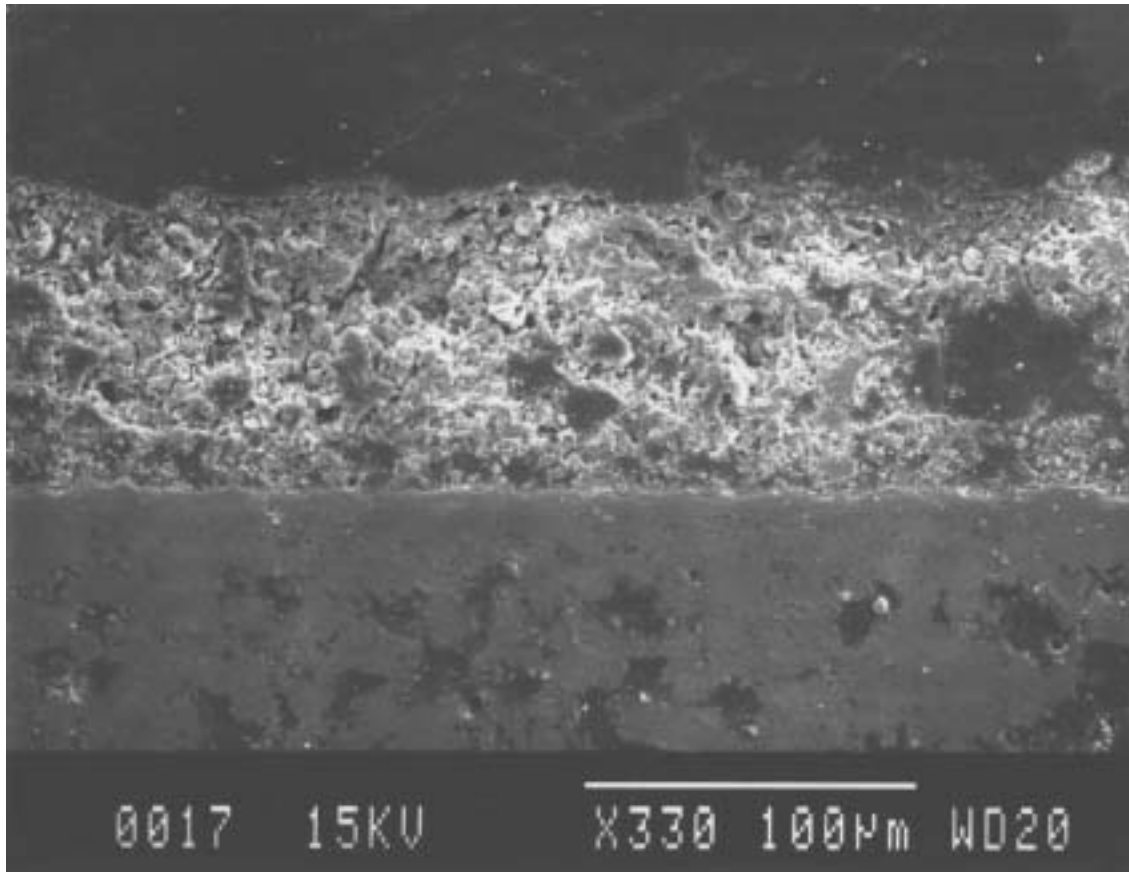
Substrate side



Solid oxide fuel cells



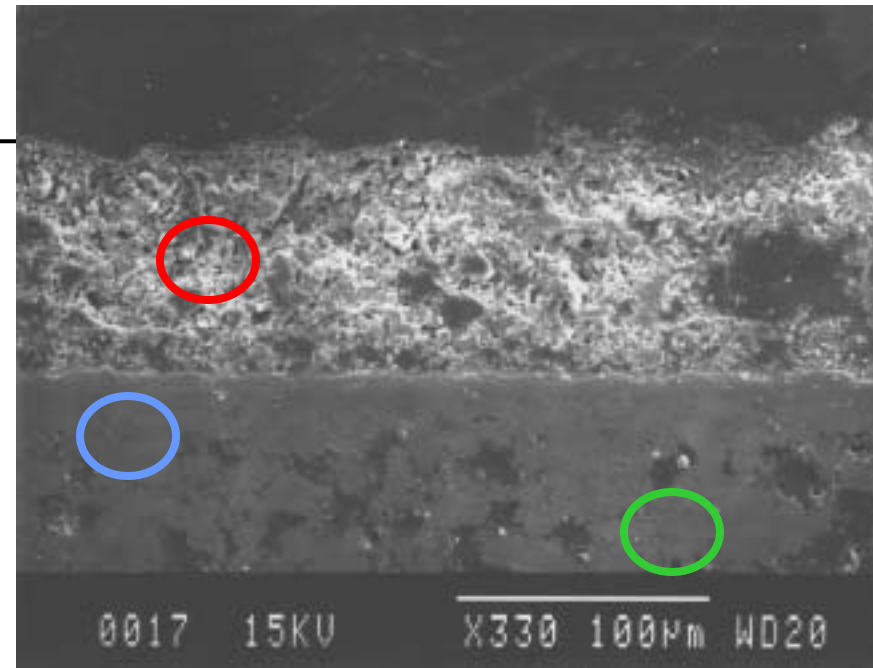
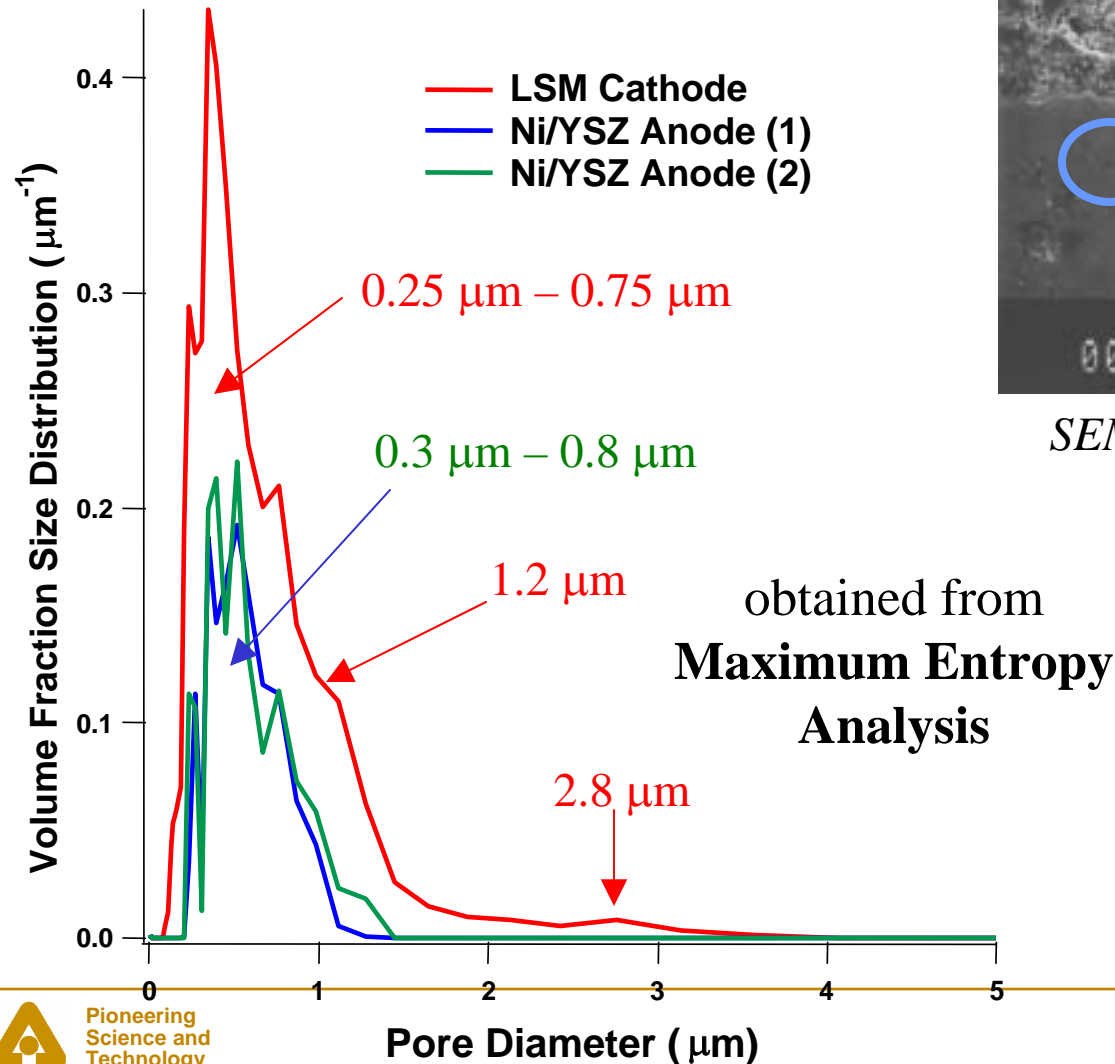
Solid oxide fuel cell microstructures



Layered structure

- Top (cathode) porous and fragile
- Thin layer of electrolyte
- Lower (anode) layer - porous

Preliminary Void Size Distributions 2-D collimated USAXS



SEM micrograph near interfaces.

Volume Fractions (%):

Cathode: 24.6

Anode (1): 10.0

Anode (2): 10.5

Surface Areas ($\text{m}^2 \text{ cm}^{-3}$):

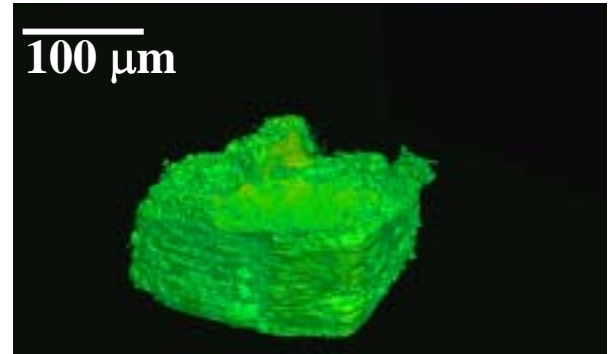
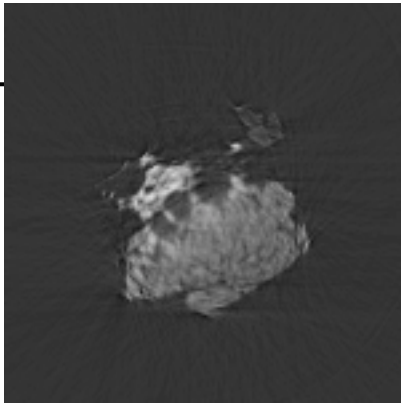
Cathode: 3.39 ± 0.01

Anode (1): 1.06 ± 0.01

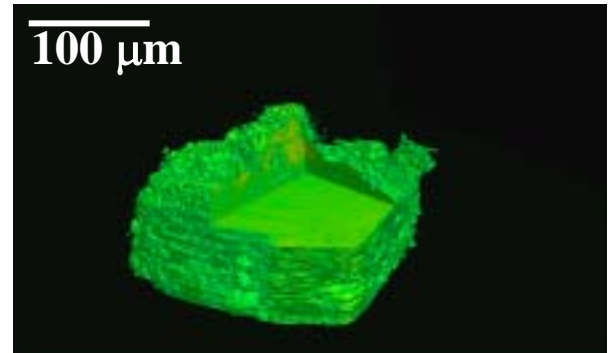
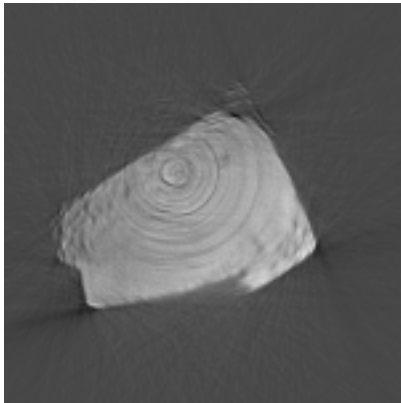
Anode (2): 1.20 ± 0.01

Microtomography of SOFCs

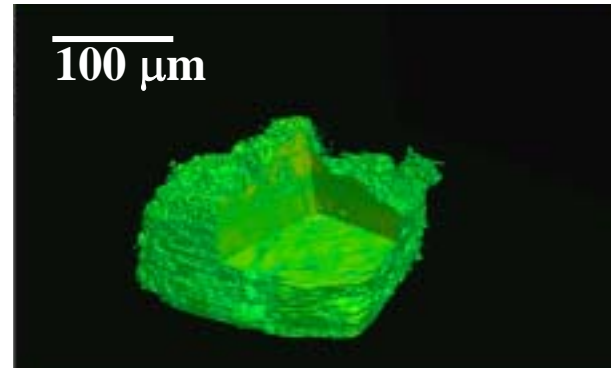
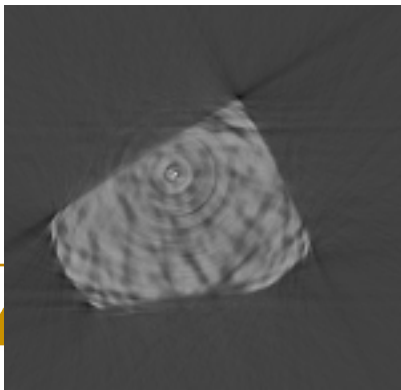
Porous LSM Cathode



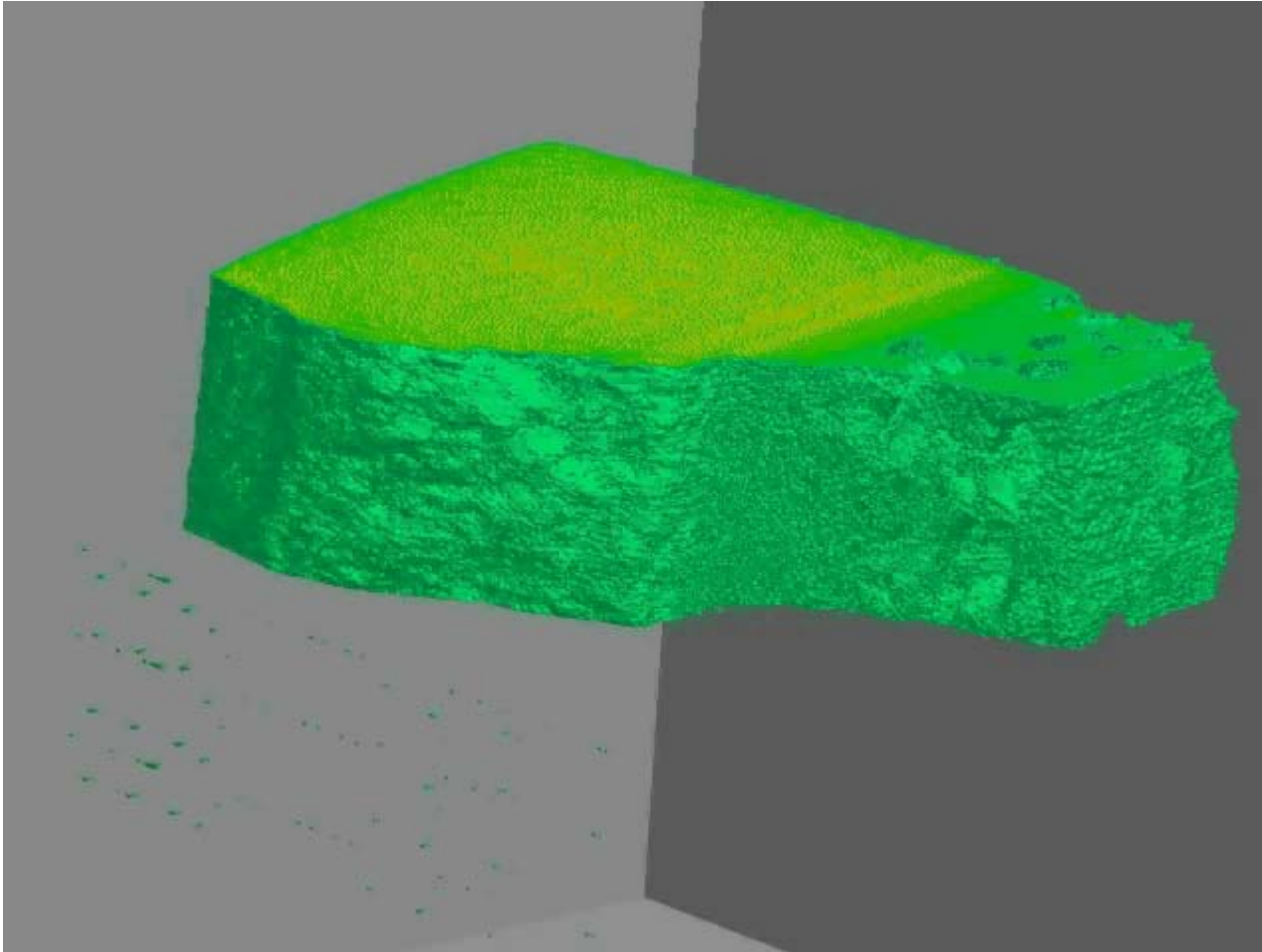
Dense YSZ Layer



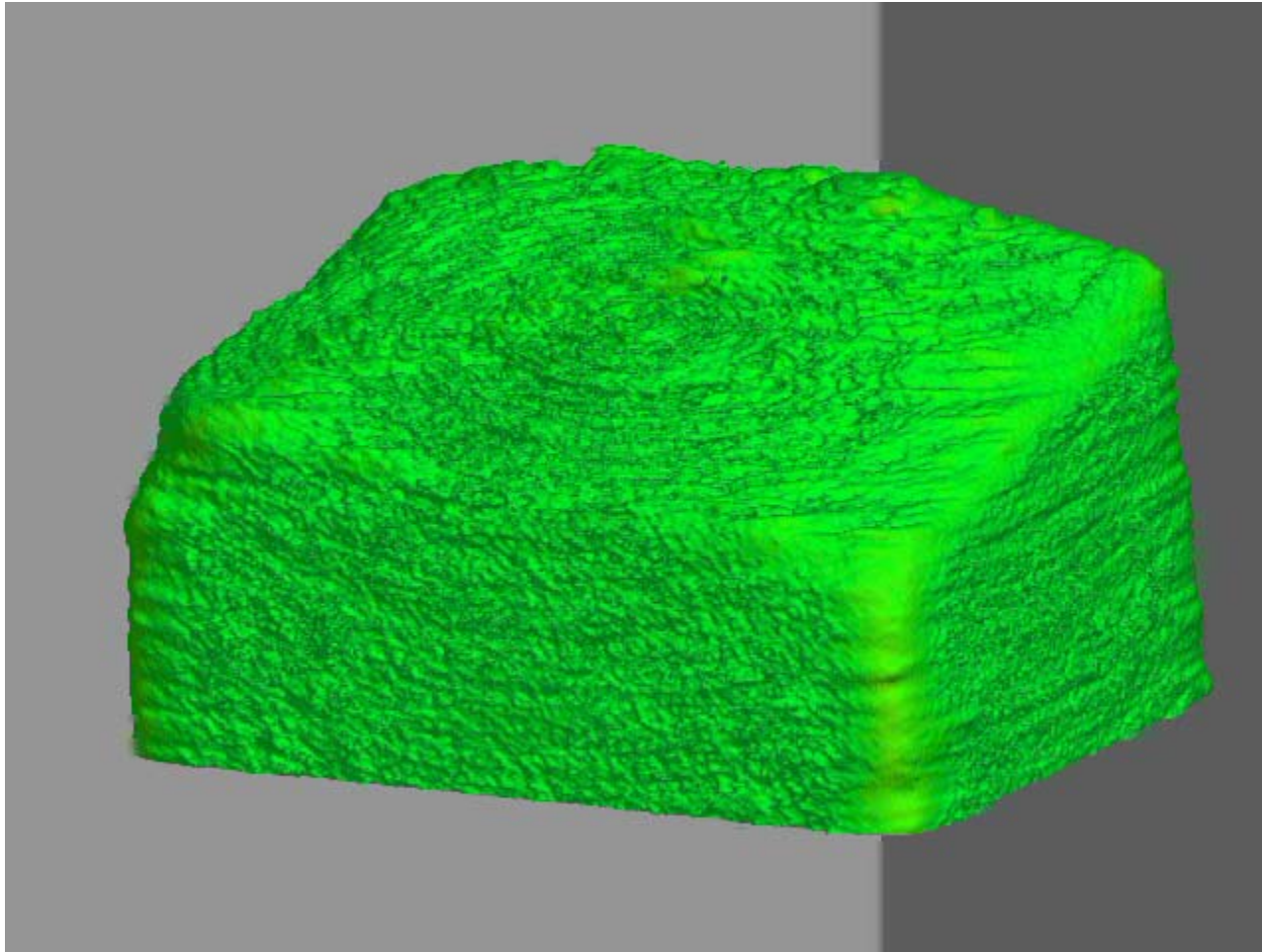
Porous Ni(YSZ) Anode



32% Anode SOFC

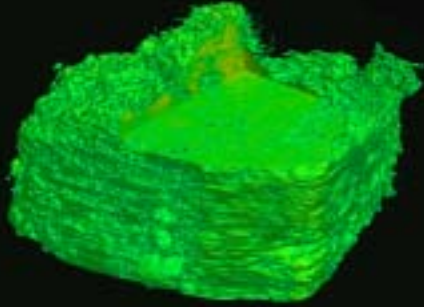


Or another view on LSM sample

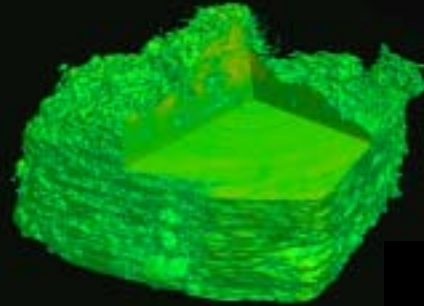


Tomography Resolution:
 $\sim 1.3 \mu\text{m}$

100 μm



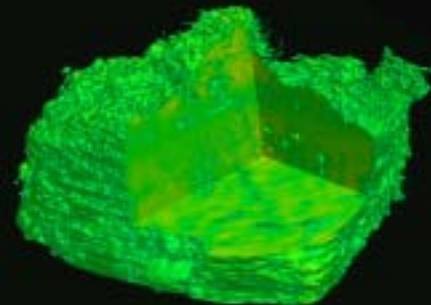
100 μm



Slices in LSM
Cathode:
Porous Layer

YSZ Electrolyte:
Dense Layer

100 μm



Slices in Ni(YSZ)
Anode:
Porous Layer

Conclusions

- **Significant development in materials characterization of advanced ceramic materials for energy applications is needed**
- **Tomography is ideal tool for characterization of voids in these complex structures. The resulting data are ideally suited as input data for computer modeling.**
- **Tomography improvements needed :**
 - Improvements in resolution (at least to 100nm, better to 10-20 nm)
 - Keeping the field of view on the current level (at least 150 – 200 micrometers)
 - Useful further features:
 - *Element specificity*
 - *In situ capabilities with furnace and chemical cell capabilities*

Wish list

- **Field of view : 200 micron x 200 micron or larger**
- **Resolution : better than 50 nanometers**
- **Energy range : 10 – 60 keV**
- **Data processing : post reconstruction analysis support**
 - De-blur, threshold, real density calibration
 - Quantitative values mining
 - Imaging 3D
- **Data manipulation : storage and handling**
- **Sample environment: furnace & chemical environment cell**
- **“One stop experiment”**
 - Pre-experiment support
 - Experiment
 - Data analysis and evaluation